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(54) HOT DIP Zn-Sn PLATED STEEL SHEET EXCELLENT IN CORROSION RESISTANCE (57)Abstract:

PROBLEM TO BE SOLVED: To provide a hot dip Zn-Sn plated steel sheet having excellent corrosion resistance and applicable to an automobile body and a building material such as a roof material and a wall material.

SOLUTION: In this hot dip Zn-Sn plated steel sheet excellent in corrosion resistance, the surface of the steel sheet has a hot dip Zn-Sn plated layer, the composition of the plated layer contains 1 to <50%, preferably, 1 to <40% Sn in addition to Zn. Further, the hot dip Zn-Sn plated steel sheet excellent in corrosion resistance contains 1 to 25% Cr in the steel. Moreover, the average value of the coating weight is 25 to 100 g/m2 per side, and the standard deviation is ≤ 4 g/m². Further, the composition of the plated layer contains one or more kinds of elements selected from 0.2 to 8% Mg and 0.02 to 5% Al in addition to Zn and Sn and moreover contains one or more kinds of elements selected from 0.1 to 5% Ca and 0.1 to 5% Li. Further, the boundary between the plated layer and the steel sheet is provided with a preplated layer containing Ni, Co, Fe, Cr, Sn, Zn and Cu, or the outermost surface of the plated layer is provided with a posttreated film.

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HOT DIP Zn-Sn PLATED STEEL SHEET EXCELLENT IN CORROSION

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ABSTRACT:

PROBLEM TO BE SOLVED: To provide a hot dip Zn-Sn plated steel sheet having excellent corrosion resistance and applicable to an automobile body and a building material such as a roof material and a wall material.

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CLAIMS

[Claim(s)]

[Claim 1] The melting Zn-Sn system plating steel plate excellent in the corrosion resistance characterized by having a melting Zn-Sn plating layer on a steel plate front face, and a plating layer presentation containing Sn less than 1 to 50% in addition to Zn.

[Claim 2] The melting Zn-Sn system plating steel plate excellent in the corrosion resistance characterized by having a melting Zn-Sn plating layer on a steel plate front face, and a plating layer presentation containing Sn less than 1 to 40% in addition to Zn.

[Claim 3] The melting Zn-Sn system plating steel plate excellent in the corrosion resistance according to claim 1 or 2 characterized by containing Cr:1-25% in steel.

[Claim 4] For the average of plating coating weight, one side 25 - 100 g/m2, and standard deviation are 4 g/m2. Melting Zn-Sn system plating steel plate excellent in the corrosion resistance according to claim 1 to 3 characterized by being the following.

[Claim 5] The melting Zn-Sn system plating steel plate excellent in the corrosion resistance according to claim 1 to 4 characterized by the presentation of a plating layer containing one sort (Mg:0.2-8% and aluminum:0.02-5%) or two sorts in addition to Zn and Sn.

[Claim 6] The melting Zn-Sn system plating steel plate excellent in the corrosion resistance according to claim 1 to 5 characterized by containing one sort (calcium:0.1-5% and Li:0.1-5%) or two sorts further in a plating layer.

[Claim 7] The melting Zn-Sn system plating steel plate excellent in the corrosion resistance according to claim 1 to 6 characterized by having a plating layer and the pre plating layer which contains nickel, Co, Fe, Cr, Sn, Zn, and Cu in the interface of a steel plate.

[Claim 8] The melting Zn-Sn system plating steel plate excellent in the corrosion resistance according to claim 1 to 7 characterized by having an after-treatment coat on the maximum front face of a plating layer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention] This invention relates to the suitable surface treated steel sheet for metal building materials, such as rust-proofing material for automobile car bodies, and a roof, a wall, etc. especially about the surface treated steel sheet which has the outstanding corrosion resistance. [0002]

[Description of the Prior Art] It is known well that Zn plating steel plate has the rust-proofing nature to a steel plate from the sacrifice corrosion prevention ability to a steel plate (griddle). However, therefore it is easy to generate white rust, and the potential difference with a steel plate also has it beyond the need, and it is not enough for long-term rust-proofing nature. On the other hand, Sn plating steel plate is mainly widely used in the food can and the drink can application from the outstanding corrosion resistance which Sn has, and workability. However, under the usual environment where oxygen exists, Sn does not have the operation which carries out the sacrifice corrosion prevention of the steel plate, and has the fault that the corrosion from a ferrite tends to advance. In order to compensate this, the Sn-Zn plating steel plate which added Zn 20 to 40% is mainly used in the post-plating field to electronic parts, autoparts, etc. (JP,6-116749,A). However, it is based on electroplating until now, and since electroplating of Sn had low current density, high coating weight was difficult at the reasons of cost and productivity.

[0003] On the other hand, this invention persons did the knowledge of having the property this Sn-Zn plating steel plate excelled [property] in the motor fuel tank application, and have indicated the melting Sn-Zn plating steel plate which sets the diameter of a coagulation pattern (spangle) to 20mm or less in Japanese Patent Application No. No. 132995 [seven to] as a rust-proofing steel plate for fuel tanks which was excellent in workability and corrosion resistance especially in the melting Sn-Zn plating steel plate which controlled the plating organization in Japanese Patent Application No. No. 69087 [seven to] etc.

[0004]

[Problem(s) to be Solved by the Invention] The above mentioned melting Sn-Zn plating steel plate is the the best for the fuel tank application of which it has the corrosion resistance which surely was excellent, workability, and weldability, and is processed into a complicated configuration, and inside-and-outside side corrosion resistance is required. However, amelioration was required for an application which requires the chemical conversion nature and about the same continuous-welding nature as Zn plating which were excellent like an automobile car body, or the application which dislikes rust generating of a steel plate amputation stump side for a building-materials application like a roof and a wall. [0005]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, this invention persons do the knowledge of examination and corrosion resistance improving further in combination with the steel component of a steel plate about the optimal presentation of Zn and Sn which is a plating layer metal, and result in this invention. That is, if Zn content which is a plating lamination

metal exceeds 50% of a plating layer, the outstanding phosphate processing (chemical conversion) nature required for automobile car-body steel materials will be demonstrated. Moreover, from a steel plate, plating layer potential is also ** and demonstrates a sacrifice corrosion prevention operation to a steel plate. Furthermore, while the corrosion resistance of the steel plate itself improves by adding Cr to a steel plate, although it is hot dipping therefore, the minute amount thermal diffusion in [Cr] steel happens into a plating layer. Thereby, much more improvement in plating layer corrosion resistance is obtained. This operation is convenient also when using this steel plate for the building materials of a roof and a wall. That is, while avoiding rust generating from an amputation stump side according to a sacrifice corrosion prevention operation of a plating layer, compared with a Zn independent plating layer, long-term edge-proof creep nature is also secured by the outstanding corrosion-resistant improvement in corrosion resistance and the steel plate itself.

[0006] Hereafter, this invention is explained to a detail. Zn in a plating layer is added for grant of the sacrifice corrosion prevention operation to a steel plate, and although based also on the environment exposed, plating layer potential is led to ** rather than a steel plate at several % or more. However, in little Zn addition, since a sacrifice corrosion prevention operation will be lost at an early stage if Zn finishes being eluted, a certain amount of Zn content is required, and, thereby, the period of sacrifice corrosion prevention becomes that much long. When using the Zn-Sn plating steel plate which is this steel plate for an automobile car body, as an important element, there is phosphate processability performed as paint pretreatment besides the nakedness corrosion resistance (non-painted corrosion resistance) which needs the corrosion resistance of a plating layer. If phosphate processability is not enough, the paint film adhesion after the lack of an electrodeposted workmanship appearance or middlecoat + finishing performed after that will become unstable. The outstanding coating is developed variously recently, and although like [before / that it is hard to be influenced of phosphate processability as it has become], formation of a healthy phosphate processing coat is certain [it] that they are coating adhesion and an element important for the corrosion-resistant reservation after paint. When Zn exceeded 50% in the experiment of this invention persons, it turned out that a healthy phosphate coat is formed. [0007] On the other hand, although it is rust proofing of a building-materials end face, rust generating which is easy to give an impression that it has truly corroded from appearance tends to be disliked. Although the hot-dip zinc-coated carbon steel sheet which is Zn generates white rust 100%, it is hard to generate rust. Only by Zn, since the rate of dissolution is quick, long-term rust proofing is not simply expectable. This invention is controlling the property and plating layer rate of dissolution of Zn, and has the end-face corrosion resistance which was excellent also in Zn independent twist. As mentioned above, the amount of Sn in a plating layer is limited to less than 1 - 50%. It is less than 1 - 40% desirably.

[0008] Moreover, in case this steel plate is used for various applications, resistance welding, such as spot welding, is carried out. At this time, in order that Cu of an electrode, a plating metal, especially Sn may tend to form a compound, the coating weight of plating influences weldability greatly. Moreover, naturally the effect on corrosion resistance of plating coating weight is also large. Advantageous in respect of corrosion resistance, although it works disadvantageously in respect of weldability, the effect of coating weight variation is so large that coating weight is large especially. Namely, although one side 20-100g/m2 (it selects according to an application) is suitable for the balance of weldability and corrosion resistance to coating weight, it makes variation standard deviation, and it is 4g/m2. Stabilization of corrosion resistance or weldability is aimed at by considering as the following. Although the gas wiping method is usually used, the effect on coating weight variation has the largest BATATSUKI of the plate at this time, for example, coating weight control is possible for reducing coating weight variation by stopping BATATSUKI of a plate with a support roll, an electromagnet, etc. under bath.

[0009] This Zn-Sn plating steel plate has the beautiful gloss appearance, and is promising also as metal building materials. In that case, the endurance over a long period of time is required. Cr addition into steel is effective and rust generating can be notably controlled by effectiveness showing up and adding 3% or more by adding Cr 1% or more. For this reason, it is desirable to add Cr 3% or more to the

application of which long-term corrosion resistance is required. If Cr is added, naturally cost will go up and workability will also be checked. As for the addition of such semantics to Cr, it is desirable that it is 25% or less. Moreover, the application of IF steel which was excellent in workability to the application of which advanced workability is required is desirable, and in order to secure the welding airtightness after welding, fabricating nature, etc. further, the steel plate which added several ppm B is desirable. To the application of which especially workability is not required, application of low-carbon steel is desirable.

[0010] Next, although a plating layer uses Zn and Sn as the base, otherwise, addition of Mg is desirable [a layer] from the semantics of corrosion resistance. A compound called Mg2 Sn is formed the inside Sn of a plating layer, this carries out the priority dissolution in corrosive environment, Mg system coat covers a plating layer and a ferrite, and Mg shows the corrosion prevention effectiveness. Since it increases several times from Sn and Zn as atomic concentration even when it is little in weight %, since Mg is a light element, effectiveness is comparatively demonstrated from small quantity. Corrosion resistance improves so that corrosion resistance improves and it adds by 0.2% or more of addition, but since melting temperature also rises on the other hand, as for an upper limit, considering as 8% is desirable. Furthermore, a certain thing is known and, as for Mg, the stabilization effect of Zn system corrosion product also demonstrates effectiveness to corrosion-resistant improvement together with the above-mentioned operation.

[0011] Mg is an element with very strong compatibility with oxygen, if it adds Mg to Zn-Sn, intense oxidation of Mg takes place by the bath surface, operation nature falls sharply, and hot dipping is impossible for it as a matter of fact. However, aluminum is effective in oxidation control of Mg, and operation nature is improved by adding aluminum which is about [of the amount of Mg] 1/10. Therefore, when adding Mg, aluminum shall also be added to coincidence, aluminum is effective also in oxidation control of Sn and Zn itself, and also when not adding Mg, a plating appearance is improved by adding aluminum. In order to demonstrate such an operation, as for aluminum, it is desirable that it is 0.02 - 5%. An upper limit is defined by melting temperature from the effectiveness as opposed to oxidation control in a minimum.

[0012] There are calcium and Li as an element which has the same operation as Mg. Sn and the compound which is easy to dissolve are formed, calcium and Li which were dissolved form a coat and these also have the corrosion prevention effectiveness. Therefore, it is also possible to also add these elements and for it to be effective for corrosion-resistant improvement, and to add 0.1 to 5%, respectively. An upper limit is defined by melting temperature from the effectiveness as opposed to corrosion resistance in the minimum of these element concentration. Each of these is elements with strong compatibility with oxygen, and aluminum is effective in the oxidation control too. There may be Fe of a minute amount as an impurity element of a plating layer. Moreover, Mg, aluminum, a misch metal, Sb, etc. may be added if needed.

[0013] Naturally it is also possible to galvanize directly to a steel plate on the occasion of plating, and it is also possible to perform pre plating processing before plating. Pre plating is performed in order to raise plating nature, and it may have a metal containing nickel, Co, Fe, Cr, Sn, Zn, Cu, or these. Although thickness is usually about 0.1 micrometers, it is not limited specially. as the hot-dipping approach -- large -- flux growth and ZENJIMA -- although there may be law, it is possible at both of the manufacturing methods. general -- the thing with high productivity -- ZENJIMA -- it is law and manufacture by this approach is more desirable.

[0014] Next, as an after-treatment coat after plating, there is a chromate film etc. and properties, such as corrosion resistance, weldability, and corrosion resistance after paint, are influenced. Although a chromate film is the thing excellent in corrosion resistance and paintwork and has so far been used abundantly, Cr6+ is harmful to the body and many after-treatment coats for which this is substituted are also devised in recent years. It is also possible to apply these after-treatment coat in this invention. As an after-treatment coat, a non clo coat is desirable, for example, a silane coupling agent-phenol resin-phosphoric-acid system coat etc. is possible.

[0015] Next, an example explains this invention to a detail further.

[Example] (Example 1) After ingoting the steel of the component shown in Table 1 by the usual converter-vacuum-degassing processing and considering as slab, hot rolling, cold rolling, and a continuous-annealing process were performed on condition that usual, and the annealing steel plate (0.8mm of board thickness) was obtained. It is nickel plating at a Watts bath to this steel plate 1 g/m2 After giving, Zn-Sn plating was performed with flux growth. Flux is ZnCl2. It was used having carried out roll coating of the water solution, and the presentation of Sn was changed among 0 - 60%. Bath temperature considers as 280-320 degrees C, and is plating coating weight by air wiping after plating One side 50 g/m2 It adjusted. These engine performance was evaluated. The evaluation approach at this time was based on the approach described below. Plating conditions and a performance-evaluation result are shown in Table 2.

[0016]

[Table 1]

表1 めっき原板の成分(wt%)

符号	С	Si	Мn	P	s	T i	ΑI	Сг	N
A	0.0030	0.09	0. 30	0.008	0.012	0. 082	0.05	0. 01	0. 0033
В	0.0015	0.05	0. 27	0.007	0. 005	0. 15	0.04	4. 88	0. 0029

[0017] (1) PB[by chemical conversion nature ** phosphating nature Nihon Parkerizing Co., Ltd.]-3020 processing was performed, and the existence of the chemical film nonuniformity after processing was observed.

[Valuation basis]

O: -- formation -- appearance-nonuniformity-less **: -- small -- x:nonuniformity size with nonuniformity -- formation -- those with partial which are not generating a crystal [0018] (2) JIS after putting in a cross-cut crack by the cutter to a sample with a dimension of 70x150mm which painted the cation mold electrodeposition paint U-80 by Nippon Paint Co., Ltd. by 20 micrometers of thickness after performing phosphate chemical conversion stated by the corrosion-resistant evaluation ** salt damage corrosion resistance above Z The salt spray test based on 2371 was performed on the 35th, and paint film bulging (the single-sided maximum bulging) from the crack section was measured. [Valuation basis]

O: -- the 1mm [of paint film bulging] or less O:paint film bulging 1 -- < -- blistering -- <=2.5mm**:paint film bulging 2.5 -- < -- blistering -- 4mm ** of <=4mmx:paint film bulging [0019] (3) Spot welding was performed by the welding condition shown under weldability, and the number of continuation RBIs of the time of the diameter of a nugget cutting 4 roott (t: board thickness) was evaluated.

[Welding condition]

welding current: -- 95% welding pressure of a Chile generating current: 200kg weld-time: -- 12 cycle electrode: -- a dome mold, tip 6phi-40R, and product made from chromium copper [a valuation basis] O: less than 400 400-750 750 continuation RBI ** **:RBI [continuation] x:continuation RBIs [0020] (4) The workability oil pressure shaping testing machine performed cup molding with the contraction ratio 2.20 using cylinder punch with a diameter of 50mm. Oiling of the trial was carried out, it was performed and the Siwa prevention force was set to 1000kg. Evaluation of workability was based on the following index.

[Valuation basis]

O: -- abnormalities-less **: -- plating -- those with x:plating exfoliation with a crack [0021] [Table 2]

					表	2					
番	原		めっき	層組成	リン酸塩	耐	蘇聯	加工	総合	備	
号	板	Zn	Mg	A 1	他	処理性	食性	接性	生	評価	考
1	Α	90	-	-	_	0	0	0	0	0	
2	Α	86	-	_	_	0	0	0	0	0	
3	Α	68	-		-	0	0	0	0	0	
4	Α	55	_	_	_	Δ	0	0	0	0	本
5	A	80	-	_		0	0	0	0	0	
6	Α	82	-	_	_	0	0	0	0	0	発
7	В	82	-	_	_	0	0	0	0	0	
8	Α	82	1.0	0. 3	_	0	0	0	0	0	明
9	A	95	1.5	0.5	-	0	0	0	0	0	
10	Α	83	5	1.5	-	Δ	0	0	0	0	例
11	A	83	_	0. 5	Ca:1.0	0	0	0	0	0	
12	A	89	_	0.5	L i : 1.0	0	0	0	0	0	
13	A	82	_	0.5	-	0	0	0	0	0	
14	A	5	_		_	×	×	×	0	×	比
15	A	45	_		-	×	×	0	0	×	較
16	A	30		-	-	×	×	Δ	0	×	例

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[0022] The result of having mainly evaluated many properties in an automobile car-body application is shown in Table 2. Zn gives sacrifice corrosion prevention ability to a plating layer, and controls iron rust. Like No.14, by the system with little content of Zn, phosphate processability is poor and, as a result, paint film bulging of paint material also has it. [large] Moreover, in order that Sn may react with the welding electrode Cu, welding RBI nature is also inferior. Paint film bulging serves as an increasing inclination, so that there are many amounts of Zn, and as for paint film bulging, neither in 32% (No.3) nor 45% (No.4), Sn can happen easily. However, many (No.3) and phosphate processability fall [Sn]. Moreover, like No.15, probably because phosphate coat generation is poor at 45%, paint film bulging also has large Zn, and corrosion resistance is falling. Although No.9, and 11 and 12 are the systems which added Mg, calcium, and Li, although there are many amounts of Zn, good corrosion resistance is shown by the effectiveness of these alloying elements. It can check that corrosion resistance improves by adding Cr in steel as No.6, as shown in 7.

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[0023] (Example 2) After ingoting the steel of the component shown in Table 3 by the usual converter-vacuum-degassing processing and considering as slab, hot rolling, cold rolling, and a continuous-annealing process were performed on condition that usual, and the annealing steel plate (08mm of board thickness) was obtained. It is nickel plating at a Watts bath to this steel plate 1 g/m2 After giving, Zn-Sn plating was performed with flux growth. Flux is ZnCl2. It was used having carried out roll coating of the water solution, and the presentation of Zn was made into 82%. Bath temperature considers as 280 degrees C, and is plating coating weight by air wiping after plating One side 70 g/m2 It adjusted. The lower appraisal method estimated the obtained Zn-Sn plating steel plate. An evaluation result is summarized in Table 4. That is, the evaluation result in a building-materials application is shown in this table 4. Each salt damage corrosion resistance is excellent. Moreover, by using Cr content steel as a base by Zn, although end-face rust-proofing nature is also good, rust generating of an edge surface part is controlled further, and synthetically high corrosion resistance is shown.

[0024] [Table 3]

総合評価

○:優れる

h c g cg b eb cg e e

表 3 めっき原板の成分 (wt%)

符号	С	S i	Мп	P	s	Ti	A 1	Cr	N
A	0.0030	0.09	0. 30	0.008	0. 012	0.082	0.05	0. 01	0. 0033
В	0. 0015	0.05	0. 27	0.007	0.005	0. 15	0.04	4. 88	0. 0029
c	0.0025	0.11	0. 33	0.010	0.008	0. 012	0.08	10. 91	0. 0025
D	0.0022	0.08	0. 31	0.008	0. 007	0. 13	0.05	17. 65	0. 0031

[0025] [Table 4]

番号	原板	塩害耐食性	暴露耐食性
1	A	0	0
2	В	0	0
3	С	· ©	0
4	D	©	0

[0026] (1) corrosion-resistant evaluation ** salt damage corrosion resistance Nihon Parkerizing Co., Ltd. make -- JISZ after putting in a cross-cut crack by the cutter to a sample with a dimension of 70x150mm which painted the cation mold electrodeposition paint U-80 by Nippon Paint Co., Ltd. by 20 micrometers of thickness after carrying out phosphate processing PB-3020 The salt spray test based on 2371 was performed on the 35th, and paint film bulging (the single-sided maximum bulging) from the crack section was measured.

[Valuation basis]

O: -- the 1mm of paint film bulging or less O:paint film bulging 1 -- < -- blistering --<=2.5mm**:paint film bulging 2.5 -- < -- blistering -- 4mm super-[of <=4mmx:paint film bulging] salt damage corrosion resistance [0027] (2) Paint was performed after the non clo system after treatment shown in the direct weathering test table 5. Paint was used as polyethylene wax content acrylic resin (clearance: 5 micrometers). It sheared in dimension of 50x200mm, and the direct weathering test was performed. The rust incidence rate from the end face after three-month progress and the surface discoloration situation were observed. [Valuation basis]

O: -- 80% ** of - 30% or more less than 70% [of - 10% or more less than 30% / of less than 10% / of rust incidence rates / O:rust incidence rates from an end face / **:rust incidence rates from an end face] x:rust incidence rates from an end face from an end face [0028] [Table 5]

表 5 後処理の条件

組成(添加量の多い順)		付	着 量
フェノール系樹脂、シランカップリング剤。	リン酸	200 mg/m²	(SiO ₂ 換算)

[0029] (Example 3) the steel of table 1A of an example 1 -- a cold-rolled plate -- using it -- ZENJIMA --Zn-18%Sn plating was performed by law. In NOF-RF type Rhine, annealing was performed so that attainment board temperature might become 820 degrees C, and the plate was cooled and it was

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immersed to the bath so that invasion board temperature might become almost the same as bath temperature. Bath temperature could be 280 degrees C. Air wiping after plating adjusted various plating coating weight. At this time, the support roll of a pair was put in into the bath, the pressing-down conditions of this roll were changed and the variation in plating coating weight was adjusted. Coating weight variation is 2 1m. The average and standard deviation were calculated by having carried out coating weight measurement of the ten points of arbitration with the fluorescent X-ray method from the plate. Moreover, the air-cooling method performed cooling. These engine performance was evaluated. The evaluation approach at this time is the same as an example 1. The performance-evaluation result in various coating weight is shown in Table 6. [0030]

[Table 6]

番	付着量(g/m²)		リン酸塩	耐 食	溶接	加工
号	平均	標準偏差	処理性	改担	性	工 性
1	25	2. 1	0	Δ	0	0
2	40	2.8	0	0	0	0
3	60	3. 5	0	0	0	0
4	100	4.7	0	0	Δ	0
5	35	5. 5	0	0	Δ	0

[0031] The effect of plating coating weight and the steel plate engine performance on the variation is shown in Table 6. If there is little coating weight, corrosion resistance runs short, and when coating weight increases, it is in the inclination for weldability to fall. If the variation in coating weight is large even if there is coating weight between them, it will become a little unstable at weldability. Therefore, the variation in coating weight is 4 g/m2 as standard deviation. It is desirable that it is the following. [0032]

[Effect of the Invention] This invention offers the melting Zn-Sn system plating steel plate excellent in corrosion resistance. Zn-Sn system plating can use variously an automobile car body, building materials like a roof and a wallplate, etc. for an application from the stable corrosion resistance, workability, etc. Moreover, the further corrosion-resistant improvement is possible by adding Cr to a steel plate. It is the ingredient which may be widely used for the area and member of which corrosion resistance is required by this.

[Translation done.]

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					4.紋百に嬉く

最終貝に続く

(54) 【発明の名称】 耐食性に優れた溶融2n-Sn系めっき鋼板

(57)【要約】

【課題】 本発明は、例えば自動車車体や屋根・壁等の 金属建材に適用される優れた耐食性を有する溶融 Zn-Sn系めっき鋼板を提供する。

【解決手段】 鋼板表面に溶融Zn-Snめっき層を有し、めっき層組成がZnに加えてSnを $1\sim50\%$ 未満望ましくは $1\sim40\%$ 未満含有することを特徴とする耐食性に優れた溶融Zn-Sn系めっき鋼板。また、鋼中に $Cr:1\sim25\%$ を含有する耐食性に優れた溶融Zn-Sn系めっき鋼板にある。さらに、めっき付着量の平均値が片面 $25\sim100$ g/m²、標準偏差が4 g/m 2 以下であること。並びにめっき層の組成がZn, Sn に加え、 $Mg:0.2\sim8\%$, $A1:0.02\sim5\%$ の 1種または2種以上を含有すること、更に $Ca:0.1\sim5\%$, $Li:0.1\sim5\%$ の1種または2種以上を含有すること、有すること。さらには、めっき層と鋼板の界面にNi, Co, Fe, Cr, Sn, Zn, Cu を含有するプレめっき層を有すること、ないしはめっき層の最表面に、後処理皮膜を有することも含む。

【特許請求の範囲】

【請求項1】 鋼板表面に溶融2n-Snめっき層を有 し、めっき層組成がZnに加えてSnを1~50%未満 含有することを特徴とする耐食性に優れた溶融Zn-S n系めっき鋼板。

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【請求項2】 鋼板表面に溶融Zn-Snめっき層を有 し、めっき層組成がZnに加えてSnを1~40%未満 含有することを特徴とする耐食性に優れた溶融Zn-S n系めっき鋼板。

【請求項3】 鋼中にCr:1~25%を含有すること 10 を特徴とする請求項1または2に記載の耐食性に優れた 溶融Ζη-Sη系めっき鋼板。

【請求項4】 めっき付着量の平均値が片面25~10 Og/m²、標準偏差が4g/m²以下であることを特 徴とする請求項1~3に記載の耐食性に優れた溶融乙n - S n 系めっき鋼板。

【請求項5】 めっき層の組成がZn, Snに加え、M g:0.2~8%, A1:0.02~5%の1種または 2種を含有することを特徴とする請求項1~4に記載の 耐食性に優れた溶融Zn-Sn系めっき鋼板。

【請求項6】 めっき層に更にCa:0.1~5%, L i:0.1~5%の1種または2種を含有することを特 徴とする請求項1~5に記載の耐食性に優れた溶融Zn - Sn系めっき鋼板。

【請求項7】 めっき層と鋼板の界面にNi,Co,F e, Cr, Sn, Zn, Cuを含有するプレめっき層を 有することを特徴とする請求項1~6に記載の耐食性に 優れた溶融Zn-Sn系めっき鋼板。

【請求項8】 めっき層の最表面に、後処理皮膜を有す ることを特徴とする請求項1~7に記載の耐食性に優れ 30 た溶融Ζη-Sη系めっき鋼板。

【発明の詳細な説明】

[0001]

【発明の属する技術分野】本発明は、優れた耐食性を有 する表面処理鋼板に関するもので、特に、自動車車体用 防錆材、屋根・壁等の金属建材等に好適な表面処理鋼板 に関するものである。

[0002]

【従来の技術】Znめっき鋼板は、鋼板(鉄板)に対す るその犠牲防食能から鋼板に対する防錆性を有すること 40 は良く知られている。しかしそれが故に白錆が発生し易 く、必要以上に鋼板との電位差も有り、長期の防錆性に は十分ではない。一方、Snめっき鋼板は、Snの有す る優れた耐食性と加工性から、食缶、飲料缶用途を主と して広く使用されている。しかしながら、Snは酸素の 存在する通常の環境下では鋼板を犠牲防食する作用がな く、地鉄からの腐食が進行しやすいという欠点がある。 これを補うため、例えば2nを20~40%添加した5 n-Znめっき鋼板が電子部品、自動車部品等への後め

749号公報)。しかし、これまでは電気めっき法によ るもので、Snの電気めっきは電流密度が低いため、コ スト、生産性上の理由で高付着量は困難であった。

【0003】一方、本発明者らは、自動車燃料タンク用 途でこのSn-Znめっき鋼板が優れた特性を有するこ とを知見し、特願平7-69087号等において、めっ き組織を制御した溶融Sn-Ζnめっき鋼板を、中でも 加工性、耐食性に優れた燃料タンク用防錆鋼板として特 願平7-132995号において凝固模様(スパング) ル) 径を20mm以下とする溶融Sn-Znめっき鋼板 を開示してきた。

[0004]

【発明が解決しようとする課題】前記した溶融Sn-Z nめっき鋼板は、確かに優れた耐食性、加工性、溶接性 を有しており、複雑な形状に加工され、かつ内外面耐食 性を要求される燃料タンク用途には最適である。しか し、自動車車体のように優れた化成処理性やZnめっき 並の連続溶接性を要求するような用途、或は屋根・壁の ような建材用途で鋼板切断端面の赤錆発生を嫌う用途に は改良が必要であった。

[0005]

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【課題を解決するための手段】本発明者らは、上記の課 題を解決するために、めっき層金属である2nとSnの」 最適組成について検討、更に鋼板の鋼成分との組合せで より一層耐食性が向上することを知見し、本発明に至っ たものである。即ち、めっき層構成金属であるΖη含有 量がめっき層の50%を越えると、自動車車体鋼材に必 要な優れたリン酸塩処理 (化成処理)性を発揮する。ま た、めっき層電位も鋼板より卑であり、鋼板に対して犠 性防食作用を発揮する。更に、鋼板にCrを添加するこ とで鋼板自体の耐食性が向上すると共に、溶融めっきで あるが故に、めっき層中に鋼中Crの微量熱拡散が起こ る。これにより一層のめっき層耐食性向上が得られる。 この作用は屋根・壁の建材に本鋼板を使用する時も好都 合である。即ち、切断端面からの赤錆発生をめっき層の 犠牲防食作用により回避すると共に、乙n単独のめっき 層に比べてその優れた耐食性と鋼板自体の耐食性向上に より、長期の耐エッジクリープ性も確保される。

【0006】以下、本発明を詳細に説明する。めっき層 中のZnは鋼板への犠牲防食作用の付与のために添加す るもので、晒される環境にもよるが、数%以上でめっき 層電位を鋼板よりも卑に導く。しかし少量の2n添加で はZnが溶出し終えると犠牲防食作用が早期に失われる ため、ある程度のZn含有が必要であり、それにより犠 性防食の期間がその分長くなる。自動車車体に本鋼板で あるZn-Snめっき鋼板を使用するとした場合、重要 な要素としては、めっき層の耐食性が必要な裸耐食性 (未塗装耐食性)の他に、塗装前処理として行われるリ ン酸塩処理性がある。リン酸塩処理性が十分でないと、 っき分野を主として使用されている(特開平6-116 50 電着仕上り外観不足やその後に行われる中塗り+上塗り

後の塗膜密着性が不安定となる。最近は優れた塗料が種々開発されており、以前よりはリン酸塩処理性の影響を受け難くなっているようようではあるが、健全なリン酸塩処理皮膜の形成は塗料密着性や塗装後耐食性確保に重要な要素であることは間違いない。本発明者らの実験でZnが50%を越えると健全なリン酸塩皮膜が形成されることがわかった。

【0007】一方、建材端面の防錆であるが、見た目からいかにも腐食しているとの印象を与え易い赤錆発生は嫌われる傾向にある。100%Z nである溶融亜鉛めっき鋼板は白錆は発生するが赤錆は発生し難い。ただZ nだけではその溶出速度が速いため長期の防錆が期待できない。本発明はZ nの特性とめっき層溶出速度を制御しており、Z n単独よりも優れた端面耐食性を有している。以上からめっき層中S n量は $1\sim50\%$ 未満に限定する。望ましくは $1\sim40\%$ 未満である。

【0008】また、本鋼板を各種用途に使用する際に は、スポット溶接等の抵抗溶接が実施される。このとき 電極のCuとめっき金属、特にSnとは化合物を形成し やすいために、めっきの付着量が溶接性へ大きく影響す 20 る。また、めっき付着量は当然耐食性への影響も大き い。付着量が大きいほど耐食性という点では有利に、ま た溶接性という点では不利に働くが、なかでも付着量バ ラツキの影響が大きい。即ち、溶接性と耐食性のバラン スから付着量は片面20~100g/m² (用途別に選 定する)が適当であるが、バラツキを標準偏差として4 g/m² 以下とすることで耐食性や溶接性の安定化を狙 う。付着量制御は通常ガスワイピング法が用いられる が、このときの板のバタツキが付着量バラツキへの影響 が最も大きく、例えば浴中のサポートロールや電磁石等 30 で板のバタツキを抑えることで付着量バラツキを低減す ることは可能である。

【0009】このZn-Snめっき鋼板は美麗な光沢外観を有しており、金属建材としても有望である。その際には長期に亘る耐久性を要求される。鋼中へのCr添加が有効で、Crを1%以上添加することで効果が現れ、3%以上添加することで赤錆発生を顕著に抑制できる。このため長期の耐食性を要求される用途へはCrを3%以上添加することが望ましい。Crを添加すると当然コストが上昇し、また加工性も阻害される。このような意40味からCrの添加量は25%以下であることが望ましい。また、高度な加工性を要求される用途へは加工性に優れたIF鋼の適用が望ましく、さらには溶接後の溶接気密性、二次加工性等を確保するためにBを数ppm添加した鋼板が望ましい。特に加工性を要求されない用途に対しては低炭素鋼の適用が望ましい。

【0010】次に、めっき層はZnとSnをベースとするが、他にMgの添加が耐食性という意味からは好ましい。Mgはめっき層中SnとMg2 Snという化合物を形成し、これが腐食環境中で優先溶解してMg系皮膜が 50

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めっき層、地鉄を覆って防食効果を示す。MgはSn, Znよりも軽元素であるため、重量%では少量でも原子 濃度としては数倍になるため比較的少量から効果を発揮 する。0.2%以上の添加で耐食性が向上し、添加する ほど耐食性は向上するが、一方、溶融温度も上昇してい くため上限は8%とすることが望ましい。更に、Mgは Zn系腐食生成物の安定化効果もあることが知られてお り、前述の作用と合せて耐食性向上に効果を発揮する。 【0011】Mgは極めて酸素との親和性の強い元素 で、Zn-SnにMgを添加すると浴面でMgの激しい 酸化が起こって操業性が大幅に低下し、事実上溶融めっ きが不可能である。しかし、Mgの酸化抑制にはA1が 有効であり、Mg量の1/10程度のA1を添加するこ とで操業性が改善される。従って、Mgを添加するとき にはAlも同時に添加するものとする。AlはSn、Z n自体の酸化抑制にも有効で、Mgを添加しないときに もAlを添加することでめっき外観が改善される。この 様な作用を発揮するためにはA1は0.02~5%であ ることが望ましい。下限は酸化抑制に対する効果から、 また上限は溶融温度から定められる。

【0012】 Mgと同様な作用を有する元素として、Ca, Liがある。これらもSnと溶解しやすい化合物を形成し、溶解したCa, Liが皮膜を形成して防食効果を有する。従ってこれら元素を添加することも耐食性向上のためには有効で、それぞれ $0.1\sim5\%$ 添加することも可能である。これら元素濃度の下限は耐食性に対する効果から、また上限は溶融温度から定められる。これらはいずれも酸素との親和性の強い元素であり、その酸化抑制にはやはりA1が有効である。めっき層の不純物元素として、微量のFeがありうる。また、必要に応じ、Mg, A1, S0 等を添加しても構わない。

【0013】めっきに際しては、鋼板に直接めっきすることも当然可能であるし、まためっき前にプレめっき処理を施すことも可能である。プレめっきはめっき性を向上させるために施すもので、Ni, Co, Fe, Cr, Sn, Zn, Cu, あるいはこれらを含有する金属が有りうる。厚みは通常0.1μm程度であるが、特別に限定するものではない。溶融めっき方法として大きくフラックス法とゼンジマー法がありうるが、どちらの製造法でも可能である。一般に生産性の高いのはゼンジマー法であり、この方法での製造がより望ましい。

【0014】次に、めっき後の後処理皮膜として、例えばクロメート皮膜等があり、耐食性、溶接性、塗装後耐食性等の特性に影響する。クロメート皮膜は耐食性と塗装性に優れたものでこれまで多用されてきたが、Cr6+は人体に有害であり、近年はこれに代替する後処理皮膜も多く考案されている。本発明においてはこれら後処理皮膜を適用することも可能である。後処理皮膜として

は、ノンクロ皮膜が好ましく、例えばシランカップリン

グ剤-フェノール樹脂-リン酸系皮膜等が有り得る。 【0015】次に実施例により本発明をさらに詳細に説 明する。

【実施例】 (実施例1)表1に示す成分の鋼を通常の転 炉-真空脱ガス処理により溶製し、鋼片とした後、通常 の条件で熱間圧延、冷間圧延、連続焼鈍工程を行い、焼 鈍鋼板 (板厚O.8mm)を得た。この鋼板にワット浴 でNiめっきを1g/m² 施した後、フラックス法でZ n-Snめっきを行った。フラックスはZnCl2 水溶* *液をロール塗布して使用し、Snの組成は0~60%の 間で変更した。浴温は280~320℃とし、めっき後 エアワイピングによりめっき付着量を片面50g/m² に調整した。これらの性能を評価した。このときの評価 方法は下に記述した方法によった。めっき条件と性能評 価結果を表2に示す。

[0016]

【表1】

表1 めっき原板の成分(wt%)

符号	С	Si	Mn	P	s	Тi	Αl	Сг	N
A	0.0030	0.09	0.30	0.008	0.012	0.082	0.05	0. 01	0. 0033
В	0.0015	0.05	0. 27	0.007	0.005	0. 15	0.04	4. 88	0. 0029

【0017】(1)化成処理性

①リン酸処理性

日本パーカライジング(株)製PB-3020処理を行 い、処理後の化成皮膜ムラの有無を観察した。

〔評価基準〕

○: 化成外観ムラなし

△:僅かにムラあり

×:ムラ大で化成結晶の生成していない部分あり

【0018】(2)耐食性評価

❶塩害耐食性

上記で述べたリン酸塩化成処理を施した後、日本ペイン ト(株)製カチオン型電着塗料U-80を膜厚20μm で塗装した寸法70×150mmの試料に対してカッタ に準拠した塩水噴霧試験を35日行い、疵部からの塗膜 膨れ(片側最大膨れ)を測定した。

〔評価基準〕

◎:塗膜膨れ1mm以下

○:塗膜膨れ1<膨れ≦2.5mm

△:塗膜膨れ2.5<膨れ≤4mm

×:塗膜膨れ4mm超

【0019】(3)溶接性

下に示す溶接条件でスポット溶接を行い、ナゲット径が※

※4√t(t:板厚)を切った時点までの連続打点数を評 価した。

〔溶接条件〕

20 溶接電流:チリ発生電流の95%

加圧力 : 200kg 溶接時間:12サイクル

電極:ドーム型, 先端6φ-40R, クロム銅製

〔評価基準〕

○:連続打点750点超

△:連続打点400~750点

×:連続打点400点未満

【0020】(4)加工性

油圧成形試験機により、直径50mmの円筒ポンチを用 ーでクロスカット疵を入れた後、JIS Z 2371 30 いて、絞り比2.20でカップ成型を行った。試験は塗 油して行い、シワ抑え力は1000kgとした。加工性 の評価は次の指標によった。

〔評価基準〕

〇:異常無し

△:めっきに亀裂有り

×:めっき剥離有り

[0021]

【表2】

					衣	Z					
番	原		めっき	層組成	(%)	リン酸塩	耐食	溶接	加工	総合	傳
号	板	Zn	Mg	ΑI	他	処理性	性	性	生	評価	考
1	A	90	-	-	-	0	0	0	0	0	
2	Α	86	_		-	0	0	0	0	0	
3	A	68	-	_	_	0	0	0	0	0	
4	Α	55	-		_	Δ	0	0	0	0	*
5	Α	80	-	-	-	0	0	0	0	0	
6	Α	82	-	_	_	0	0	0	0	0	発
7	В	82	_	_		0	0	0	0	0	
8	Α	82	1.0	0.3	-	0	0	0	0	0	明
9	A	95	1.5	0.5	_	0	0	0	0	0	
10	A	83	5	1.5	_	Δ	0	0	0	0	例
11	A	89	_	0.5	Ca:1.0	0	0	0	0	0	
12	A	89	_	0.5	L i : 1.0	0	0	0	0	0	
13	Α	82	- .	0.5	-	0	0	0	0	0	
14	A	5	-	_	_	×	×	×	0	×	比
15	A	45	-	_	_	×	×	0	0	×	較

総合評価 〇:優れる △:やや劣るが使用可 ×:使用不可

【0022】表2に主として自動車車体用途における諸 特性を評価した結果を示す。Znはめっき層に犠牲防食 能を付与し、鉄の赤錆を抑制する。No. 14のように Znの含有が少ない系ではリン酸塩処理性が不良であ り、その結果塗装材の塗膜膨れも大きい。また、Snが 溶接電極Cuと反応するため溶接打点性も劣る。Zn量 が多いほど塗膜膨れは増大する傾向となり、Snが32 起こり難い。しかし、Snが多くなる(No.3)とリ ン酸塩処理性が低下してくる。また、No. 15のよう にZnが45%ではリン酸塩皮膜生成が不良であるため か塗膜膨れも大きく耐食性が低下している。No.9, 11, 12はMg, Ca, Liを添加した系であるが、 これら添加元素の効果で Z n 量が多いにも関わらず良好 な耐食性を示している。No. 6と7に示すように鋼中 にCrを添加することで耐食性が向上するのが確認でき る。

16 A 30

*【0023】(実施例2)表3に示す成分の鋼を通常の 転炉-真空脱ガス処理により溶製し、鋼片とした後、通 常の条件で熱間圧延、冷間圧延、連続焼鈍工程を行い、 焼鈍鋼板(板厚08mm)を得た。この鋼板にワット浴 でNiめっきを $1g/m^2$ 施した後、フラックス法でZn-Snめっきを行った。フラックスはZnCl2 水溶 液をロール塗布して使用し、Znの組成は82%とし % (No. 3) や45% (No. 4) の方が塗膜膨れは 30 た。浴温は280℃とし、めっき後エアワイピングによ りめっき付着量を片面70g/m² に調整した。得られ たZn-Snめっき鋼板を下の評価法で評価した。評価 結果を表4にまとめる。すなわち、この表4に、建材用 途における評価結果を示す。塩害耐食性はいずれも優れ ている。またZnにより端面防錆性も良好であるが、C r含有鋼を素地として使用することで、更に端面部の赤 錆発生が抑制され、総合的に高い耐食性を示す。

 $\times |\Delta|O| \times |\Theta|$

[0024]

【表3】 表 3 めっき原板の成分 (w t %)

符号	С	Si	Mn	P	s	Ti	Αl	Cr	N		
Α	0. 0030	0. 09	0.30	0.008	0. 012	0.082	0.05	0. 01	0. 0033		
В	0. 0015	0. 05	0. 27	0. 007	0, 005	0. 15	0.04	4. 88	0.0029		
С	0.0025	0.11	0. 33	0. 010	0.008	0. 012	0.08	10. 91	0. 0025		
D	0.0022	0.08	0. 31	0.008	0. 007	0. 13	0.05	17.65	0. 0031		

[0025]

*【表4】

番号	原板	塩害耐食性	暴露耐食性
1	A	0	0
2	В	0	0
3	С	©	0
4	D	0	0

【0026】(1)耐食性評価

O塩害耐食性

日本パーカライジング(株)製リン酸塩処理PB-30 20を実施した後、日本ペイント(株)製カチオン型電 着塗料U-80を膜厚20μmで塗装した寸法70×1 50mmの試料に対してカッターでクロスカット疵を入 れた後、JISZ 2371に準拠した塩水噴霧試験を 35日行い、疵部からの塗膜膨れ(片側最大膨れ)を測 定した。

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〔評価基準〕

◎:塗膜膨れ1mm以下

○:塗膜膨れ1<膨れ≦2.5mm</p>

△: 塗膜膨れ2. 5<膨れ≤4 mm

※×: 塗膜膨れ4mm超塩害耐食性

【0027】(2)屋外暴露試験

表5に示すノンクロ系後処理の後、塗装を行った。塗装 は、ポリエチレンワックス含有アクリル系樹脂(クリ $T: 5\mu m$) とした。寸法 $50 \times 200 mm$ に剪断し、 屋外暴露試験を行った。3ヶ月経過後の端面からの赤錆 発生率、表面の変色状況を観察した。〔評価基準〕

◎:端面からの赤錆発生率10%未満

○: 端面からの赤錆発生率10%以上~30%未満

20 △: 端面からの赤錆発生率30%以上~70%未満

×: 端面からの赤錆発生率80%超

[0028]

【表5】

表5 後処理の条件

組成(添加量の多い順)		付	着 量
フェノール系樹脂、シランカップリング剤	リン酸	200 mg/m³	(SiO ₂ 換算)

【0029】(実施例3)実施例1の表1Aの鋼を冷延 施した。NOF-RFタイプのラインで、到達板温が8 20℃となるよう焼鈍を行い、侵入板温がほぼ浴温と同 じになるよう板を冷却して浴へ浸漬した。浴温は280 ℃とした。めっき後エアワイピングによりめっき付着量 を種々調整した。このとき浴中へは一対のサポートロー ルを入れており、このロールの圧下条件を変えてめっき★

★付着量のバラツキを調整した。付着量バラツキは1 m² 板を使用し、ゼンジマー法でZn-18%Snめっきを 30 の板から任意の10点を蛍光X線法で付着量測定して平 均値と標準偏差を計算した。また冷却は空冷方式で行っ た。これらの性能を評価した。このときの評価方法は実 施例1と同じである。種々の付着量での性能評価結果を 表6に示す。

[0030]

【表6】

付着量(g/m²) リン酸塩 エ 食 接 号 平均 標準偏差 処理性 件 性 性 1 25 2. 1 0 0 0 2 40 2.8 0 0 0 \circ 3 60 3.5 0 0 0 0 4 100 4.7 0 0 0 Λ 0 0 5.5 0 35

【0031】表6にめっき付着量とそのバラツキの鋼板 ☆し、付着量が増大すると溶接性が低下する傾向にある。 性能への影響を示す。付着量が少ないと耐食性が不足 ☆50 付着量がその間にあっても付着量のバラツキが大きいと 11

溶接性にやや不安定となる。従って付着量のバラツキは 標準偏差として 4 g/m^2 以下であることが望ましい。 【0032】

【発明の効果】本発明は、耐食性に優れた溶融Zn-Sn系めっき鋼板を提供するものである。Zn-Sn系め

っきはその安定した耐食性、加工性等から自動車車体や 屋根・壁材のような建材などの種々用途に使用できる。 また、鋼板にCrを添加することで更なる耐食性向上が 可能である。これにより耐食性を要求される地域や部材 に広く使用され得る材料である。

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